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Investigation of intrinsic defects and their distribution in CdSe/ZnSe quantum dot structures

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Abstract

The intrinsic defects and their distribution in CdSe/ZnSe self-assembled quantum dot heterostructures grown under variation of VI/II group beam pressure ratio are investigated by luminescent and high-resolution X-ray diffraction methods. In all samples the self-activated emission connected with donor-acceptor pairs $V_{Zn}-D$ is found. Analysis of excitation spectra of this band shows that vacancy related defects are mainly localised in ZnCdSe wetting layer. It is found that increase of Se beam pressure results in: (i) the increase of the number of metal vacancy related defects and their appearance on nanoisland interface; (ii) enhancement of Cd/Zn interdiffusion process; (iii) the decrease of Cd content in nanoislands and suppression of nanoisland formation. It is proposed that observed transformation of nanoisland emission band is mainly caused by enhancement of interdiffusion process.

Keywords: Molecular beam epitaxy; II–VI semiconductors; Quantum dots; HRXRD; PL

1. Introduction

The CdSe/ZnSe self-assembled quantum dot heterostructures have been intensively investigated during the last years because of their possible application for short-wavelength optoelectronic devices [1].

Unlike well-studied III–V system the process of CdSe/ZnSe quantum dot (nanoisland) formation is more complicated and is strongly affected by Cd/Zn interdiffusion and Cd segregation [2]. Cd/Zn interdiffusion has to result into spreading of both wetting layer and nanoislands, while Cd segregation helps in nanoisland growth.

It was found that the increase of VI/II group beam pressure ratio hampers the formation of molecular beam epitaxy (MBE)-grown ZnCdSe nanoislands [3]. It was supposed to be due to suppression of segregation process as it was observed in III–V compounds [4]. At the same time the increase of Se beam pressure can stimulate the generation of intrinsic point defects that can enhance the interdiffusion processes and influence therefore the nanoisland formation. So, in the present work a spatial distribution of intrinsic defects and their influence on the optical characteristics of nanoislands in CdSe/ZnSe heterostructures were investigated.

2. Experimental procedure

The structures studied were grown on GaAs (001) substrates by MBE and contained 12 vertically stacked CdSe inserts separated by ZnSe spacers of thickness about 15 nm. Nominal thickness of CdSe inserts was two or three monolayers (ML). All samples were grown on a 200-nm thick ZnSe buffer layer and capped by a 100-nm thick ZnSe layer. ZnSe buffer and ZnSe barriers were grown at the temperatures of 280 and 230 °C, respectively. To stimulate the process of 3D island formation after the deposition of each CdSe layer the Cd beam was blocked and the structure was heated up to 340 °C and then cooled down to 230 °C under Se flux. The reflection high-energy electron diffraction was used for in situ control of the transition from two-dimensional to three-dimensional growth mode. VI/II group beam pressure ratio was 2:1 or 5:1 (low and high Se beam pressure, respectively).

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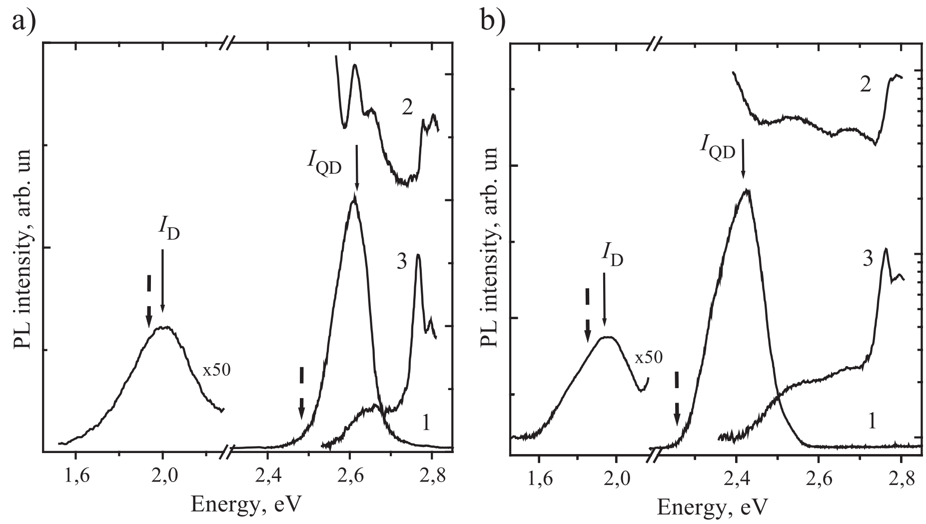

Fig. 1. PL spectra (curves 1), excitation spectra of I_{QD} (curves 2) and I_D bands (curves 3) for CdSe/ZnSe quantum dot structures with 2 ML (a) and 3 ML (b) CdSe inserts grown under VI/II beam pressure ratio of 2:1. $T = 77$ K, $\lambda_{exc} = 337$ nm. The detection energies are marked by dashed arrows.

Photoluminescence (PL) and photoluminescence excitation spectra were measured at 77 K. Photoluminescence was excited by 337 nm line of N_2-laser. For PL excitation measurements a glow lamp was used. The high-resolution X-ray diffraction (HRXRD) measurements were carried out using a X-ray diffractometer Philips MRD with a 4 × Ge (220) monochromator and Cu anode.

3. Experimental results

PL spectra of two groups of heterostructures grown under low and high Se beam pressure are shown on Figs. 1 and 2, respectively.

Fig. 1 shows PL spectra (curves 1) of two structures with CdSe inserts of nominal thickness of 2 (Fig. 1a) and 3 ML (Fig. 1b) grown under low Se beam pressure. PL spectra consist of intense emission band I_{QD} caused by radiative recombination of ground state heavy-hole-like exciton in nanoislands [5] and broad defect related band I_D. Our previous investigations have shown [6] that I_D band is the self-activated emission connected with donor-acceptor pairs V_{Zn}–D and is caused by radiative transition of electron from conduction band to an acceptor level.

The increase of the nominal thickness of CdSe insert results in the low energy shift of I_{QD} band. It is ascribed to the rise of Cd content both in ZnCdSe nanoislands and ZnCdSe wetting layer [2].

The excitation spectra of I_{QD} and I_D bands are shown in Fig. 1 by curves 2 and 3, respectively. In both spectra the features connected with the fundamental absorption edge of ZnSe layers (~ 2.8 eV) and the light absorption in ZnCdSe

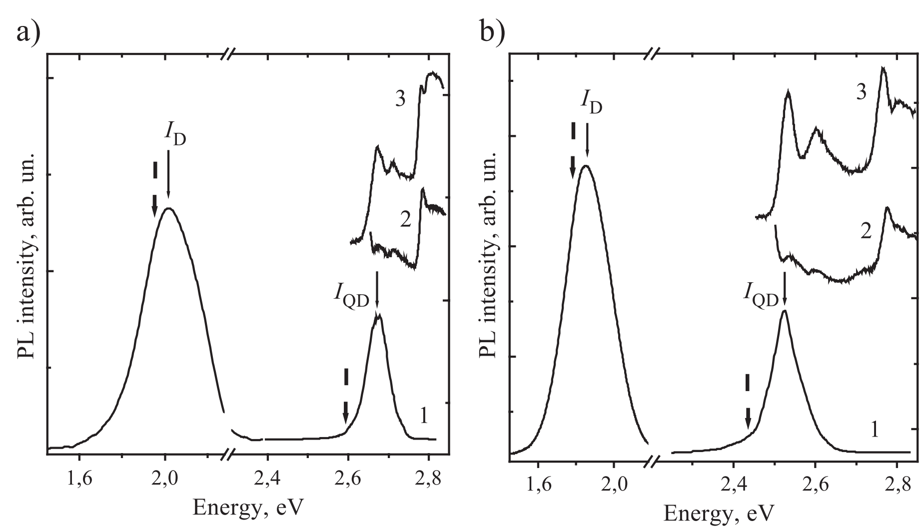

Fig. 2. PL spectra (curves 1), excitation spectra of I_{QD} (curves 2) and I_D bands (curves 3) for CdSe/ZnSe quantum dot structures with 2 ML (a) and 3 ML (b) CdSe inserts grown under VI/II beam pressure ratio of 5:1. $T = 77$ K, $\lambda_{exc} = 337$ nm. The detection energies are marked by dashed arrows.

wetting layer are observed. In addition, in the excitation spectra of I_{QD} band of the sample containing 2 ML CdSe inserts a new peak, which practically coincides with I_{QD} band position appears. It is natural to ascribe this maximum to the light absorption in nanoislands [7].

PL spectra of two structures with CdSe inserts of nominal thickness of 2 and 3 ML grown under high Se beam pressure are shown in Fig. 2a and b, respectively. The increase of VI/II group beam pressure ratio leads to the increase of I_D band intensity more than an order of value. Simultaneously I_{QD} band shifts to a high-energy region and its half-width decreases.

The increase of Se beam pressure results also in transformation of PL excitation spectra. Now the peak caused by the light absorption in nanoislands is observed in all PL excitation spectra. This peak is more pronounced in the excitation spectra of defect related band.

In PL spectra measured at high excitation level in addition to I_{QD} and I_D bands a weak emission I_{ZnSe} caused by free carrier recombination in ZnSe layers appears [8]. The spectral position of I_{ZnSe} band depends on both VI/II group beam pressure ratio and nominal thickness of CdSe insert. As Fig. 3 shows, in the samples grown under high Se beam pressure I_{ZnSe} band shifts to low energy side and widens with the increase of CdSe nominal thickness. However, simultaneous decrease of Se beam pressure reduces this shift. It should be noted, that for all structures studied a shift of I_{ZnSe} band position is accompanied by corresponding shift of the ZnSe fundamental absorption edge in the excitation spectra of both I_{QD} and I_D bands.

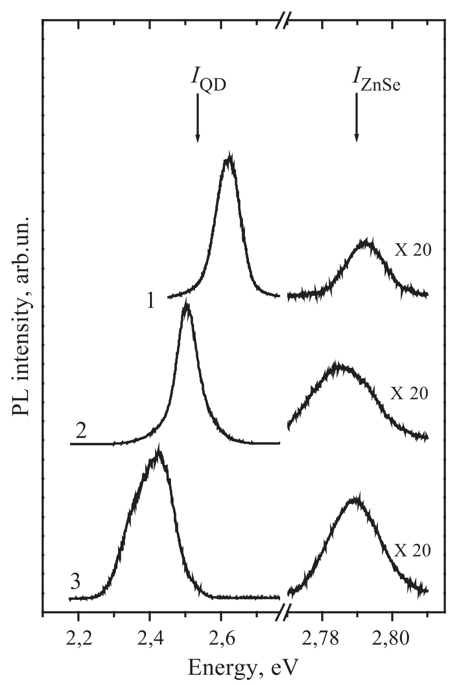

Fig. 3. PL spectra of CdSe/ZnSe quantum dot structures with 2 ML (curve 1) and 3 ML (curves 2 and 3) CdSe inserts grown under VI/II beam pressure ratio of 2:1 (curve 3) and 5:1 (curves 1 and 2). $T = 77$ K, $\lambda_{exc} = 337$ nm.

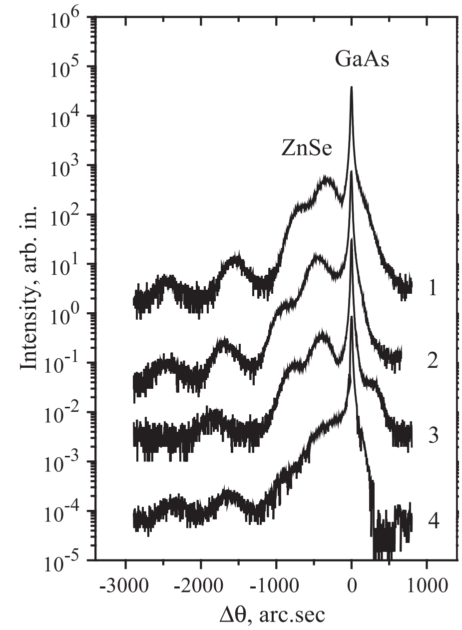

Fig. 4. Measured $\omega/2\theta$-scans of CdSe/ZnSe quantum dot structures with 2 ML (curves 1 and 3) and 3 ML (curves 2 and 4) CdSe inserts grown under VI/II beam pressure ratio of 2:1 (curves 1 and 2) and 5:1 (curves (3 and 4).

Experimental HRXRD $\omega/2\theta$-scans (004-reflection) of the samples grown under low and high Se beam pressure are shown in Fig. 4. On the low angle side from the substrate peak the signal from ZnSe layers is found. All diffraction profiles are modulated by interference. Interference fringes observed are due to phase shift induced by the CdSe layers [9]. For the structures grown under low Se beam pressure (curves 1 and 2 in Fig. 4) the increase of CdSe nominal thickness from 2 to 3 ML results into slight smearing of interference pattern. Smearing of interference pattern with the increase of CdSe nominal thickness is a typical situation for CdSe/ZnSe quantum dot heterostructures and is explained by the increase of the stacking fault density introduced in ZnSe layers because of strain relaxation [10].

For the samples grown under high Se beam pressure the clear interference pattern is observed only for the sample with 2 ML CdSe insert (curve 3 in Fig. 4). For the sample with 3 ML CdSe insert (curve 4 in Fig. 4) the smearing of interference fringe is much more pronounced in comparison with the similar sample grown under low Se beam pressure (curve 2 in Fig. 4).

The measured diffraction profiles were evaluated using simulations based on semikinematical diffraction theory [11]. The simulations show the widening of ZnCdSe layer and its depletion with Cd. These effects are more pronounced in the samples grown under high Se beam pressure. For example, in the samples with 3 ML CdSe insert the increase of VI/II beam pressure ratio from 2:1 to 5:1 results in both the decrease of Cd content in $Zn_{1-x}Cd_xSe$ layer from $x = 0.7$ down to $x = 0.3$–0.5 and increase of layer thickness from 1.2 up to 2.3 nm, respectively.

4. Discussion

Numerous transmission microscopy investigations [2,12] have shown that during the growth CdSe insert transforms into relatively wide ZnCdSe wetting layer containing two types of nanoislands: the islands with lateral dimensions < 10 nm (nanoislands of type A) and the islands with lateral dimensions 15–30 nm (nanoislands of type B). The type B islands in addition to higher dimensions contain higher Cd concentration than type A ones. The nanoislands of type A are formed even at submonolayer thickness of CdSe insert and can be considered as fluctuations of quantum well. The nanoislands of type B appear when the critical thickness of CdSe layer on ZnSe (approximately 2 ML) is reached and are assigned to a Stranski–Krastanow growth process.

As it follows from Fig. 1, our samples grown under low Se beam pressure also contain two types of nanoislands. Exciton recombination in type A nanoislands dominates in the PL spectra of the samples with 2 ML CdSe inserts, while emission from type B islands prevails in the case of 3 ML inserts. It becomes apparent from the excitation spectra of I_{QD} band of these two samples. In the case of type A islands the excitation spectrum of I_{QD} band contains the peak caused by optical transition corresponded to ground state heavy-hole-like exciton in nanoislands (Fig. 1a) while in the case of type B islands such transition is absent (Fig. 1b). Additional evidence of type B nanoisland formation in the samples with 3 ML CdSe inserts is a broadening of I_{QD} band (Fig. 1b).

However, in the samples grown under high Se beam pressure even at 3 ML thickness of CdSe inserts the nanoislands of type A arise predominantly (Fig. 2b). It is confirmed by the presence of the feature caused by the light absorption in nanoislands in the excitation spectrum of I_{QD} band as well as by I_{QD} band smaller half-width. As a rule more high-energy position of nanoisland emission band is connected with a smaller Cd concentration in nanoislands [2]. Thus, we can suppose that observed change of nanoisland emission band with the increase of Se beam pressure is caused by the decrease of Cd content in nanoislands and suppression of type B nanoisland formation.

In [3] the similar change of nanoisland emission band was supposed to be due to suppression of Cd segregation. However, Cd/Zn interdiffusion can produce the same effect. Significant enhancement of interdiffusion processes can be expected in the case of high concentration of metal vacancies [13]. Our investigations show that high number of metal vacancies is generated in the case of high Se beam pressure. It manifests itself in significant increase of vacancy related band intensity. Thus, we can expect essential enhancement of interdiffusion processes.

On the other hand, interdiffusion efficiency has to depend on localization of metal vacancies. In the excitation spectra of I_D band of all the samples the features connected with the light absorption in ZnSe layers and wetting ZnCdSe layers are observed. In the samples grown under high Se beam pressure the feature corresponded to the light absorption in nanoislands is found in addition. It indicates that vacancy related defects generated in ZnCdSe layer are mainly localised in the wetting layer. In the case of high number of these defects they are observed also on nanoisland interface. Presence of metal vacancies in wetting layer as well as on nanoisland interface can stimulate the spreading not only of wetting layer but of nanoislands also.

Cd diffusion into ZnSe layers has to manifest itself in the change of their structural and optical characteristics. It should result in formation of regions enriched with Cd in ZnSe layers adjacent to ZnCdSe insert. Such regions enriched with Cd can be either ZnSe layers doped with cadmium isovalent impurity or low concentration ZnCdSe solid solution. Their formation has to result in the low energy shift and widening of ZnSe band-to-band emission.

We indeed observed such changes of this band. In fact, in the samples contained high number of metal vacancies the increase of CdSe nominal thickness results in the low energy shift of I_{ZnSe} band and its half-width increase (Fig. 3, curves 1 and 2). It can be assigned to interdiffusion process because: (i) the increase of CdSe nominal thickness should result in the increase of Cd concentration in the insert [2]; (ii) more intense penetration of Cd in ZnSe layers can be expected because of greater concentration gradient. The increase of Se beam pressure leads to the same results. It testifies to the enhancement of diffusion process in the samples contained higher number of metal vacancy related defects.

The changes of ZnSe band-to-band emission characteristics correlate with the smearing of interference fringes in X-ray diffraction profiles that also can be explained by interdiffusion process. Indeed, the simulation of X-ray diffraction profiles shows the significant widening of ZnCdSe layer in the samples grown under high Se beam pressure.

Thus, observed changes in optical and structural characteristics of ZnSe layers indicate the enhancement of interdiffusion process with the increase of Se beam pressure. Decrease of Cd concentration in nanoislands can explain a high-energy shift of I_{QD} band.

5. Conclusion

In the present work intrinsic defects and their influence on optical characteristics of CdSe/ZnSe quantum dot heterostructures were studied by photoluminescence, photoluminescence excitation and HRXRD methods. In all samples the self-activated emission connected with donor–acceptor pairs V_{Zn}–D was observed. Analysis of excitation spectra of this band revealed that vacancy related defects are mainly localised in ZnCdSe wetting layer. In the case of high number of these defects they are observed also on nanoisland interface. Increase of VI/II beam pressure ratio from 2:1 to 5:1 results in significant change of all emission bands in photoluminescence spectra: (i) a high energy shift and narrowing of nanoisland emission band, (ii) the increase of vacancy related band intensity more than an order of value, (iii) a low energy shift and widening of ZnSe band-to-band emission peak. Simultaneously the smearing interference fringes in X-ray diffraction profiles are observed. We attribute the changes observed in PL spectra and X-ray diffraction profiles to the enhancement of Cd/Zn interdiffusion process due to increase of metal vacancy defect number. However, we cannot exclude completely the simultaneous suppression of Cd segregation.

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